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FOR
METAL COATED FIBER MATERIALS

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[Title of the Invention]

METAL COATED FIBER MATERIALS

[Field of the Invention]

This invention relates to an electrically conductive fiber material suitable for use as electromagnetic interference (EMI) shielding, grounding and other electrically conductive parts.

[Background of the Invention]

Electrically conductive fabrics have been widely used in various electronic apparatus to prevent leakage of electromagnetic waves from the apparatus. Among them is fabric of synthetic fiber, made of polymer material such as polyester or nylon, with a metal coating formed on its surface, which is characterized by its two combined characteristics - flexibility from its fiber component and EMI shielding performance from its metal component - finding wide application in the field of gaskets and tapes to be built into electronic apparatus.

The recent development of electronic apparatus reduced in size and increased in frequency has required the development of electrically conductive materials, such as EMI shielding and grounding materials, smaller in thickness and more effective especially in a high frequency region. It is known that metal foil and polymer film coated with metal by deposition or sputtering meet these requirements. Such materials, however, have the disadvantages of being lacking

in durability, flexibility and softness, which are properties required for their use as EMI shielding and other electrically conductive materials.

JP64-30899A discloses a non-woven fabric for use as an EMI shielding sheet material obtained by bonding a metal plated fiber with a flat cross-section and a thermally melting binder fiber together by melting of said binder fiber. However, this non-woven fabric bases its improved shielding performance on the thermal compression binding of the thermally melting binder fiber to the metal plated fiber, which adversely affects its flexibility and also requires extra steps making its manufacture expensive.

JP8-291432A discloses a flexible woven fabric effective in shielding EMI obtained from a metal monofilament with a flat non-round section spirally wound onto a core yarn composed of 10 or more fibers. This fabric, however, has the disadvantage of requiring an increased amount of the metal monofilament to obtain a satisfactory EMI shielding effect, which, in turn, adversely influences its flexibility, as well as its cost performance.

[Object of the Invention]

The present invention has been made against the background of the prior art involving the above-mentioned technical problems. It is therefore an object of the present invention to provide an electrically conductive fabric, which maintains the flexibility of its fiber substrate and has high

EMI shielding performance over a broadband, finding wide application in the field of electrically conductive materials such as EMI shielding and grounding.

[Summary of the Invention]

The present invention primarily resides in an electrically conductive fiber material which comprises a fabric constructed of multifilament yarn composed of a plurality of flat thermoplastic singlefilaments and a metal coating layer formed on the surface of the fabric.

The present invention secondarily resides in a method for producing an electrically conductive fiber material which comprises providing a fabric constructed of multifilament yarn composed of a plurality of thermoplastic flat single filaments and subjecting the fabric to a metal coating treatment.

The fabric particularly preferable in the present invention is a woven fabric. The flat singlefilament particularly preferable according to the present invention has an average flat ratio of 1.5 to 5.0. The multifilament useful in constructing the fabric of the present invention has an average compression of 1.0 to 8.0, preferably 1.2 to 7.0. The warp of useful fabric according to the present invention preferably has a fabric surface occupancy ratio of 60 to 90%, while its weft preferably has a fabric surface occupancy ratio of 90 to 120%. The fabric according to the present invention preferably has a cover factor of 1000 to

3000. The thermoplastic polymer composing the multifilament yarn of fabric useful in the present invention preferably is polyester.

[Preferred Embodiments of the Invention]

According to the present invention, fabric constructed of multifilament yarn composed of a plurality of flat thermoplastic singlefilaments is coated with metal to manufacture an electrically conductive fiber material.

The fiber material constructed of such multifilament yarn composed of flat singlefilaments according to the present invention includes, without limitation, woven fabric, knitted fabric and non-woven fabric. Among these fabrics, however, woven fabric is preferable for the present invention, because it can yield an electrically conductive material which is advantageous in thinness, high EMI shielding performance and ease of processing into secondary products.

Useful woven fabric of the present invention may be manufactured using the multifilament composed of flat singlefilaments, as referred to in the present invention, for its warp or weft alone, or both thereof, whether in part or whole. The weave of woven fabric according to the present invention includes, without limitation, plain, twill and satin, and any combination thereof. Among these weaves, however, plain weave is preferable for the present invention because it is advantageous in mechanical properties, yarn

fray resistance and thinness.

The average flat ratio of a flat singlefilament useful in manufacturing electrically conductive fiber material of the present invention refers to the value determined by drawing a rectangle circumscribed along the cross-section of the flat singlefilament as illustrated in Fig. 1 and dividing the long side (L) of the rectangle by its short side (S), which is normally in the range of 1.5 to 5, preferably 2 to 4. As found in the process of the present invention, a flat singlefilament with an average flat ratio of more than 5 has a problem with its processing into multifilament yarn and fabric, while the one, whose average flat ratio is 1.5 or below, causes a problem with the flexibility of the electrically conductive fabric resulting from it. To eliminate these problems, the flat singlefilament of the present invention has a cross-section, the circumscribed rectangle of which has normally a long side (L) of 10 to 50 μm , preferably 20 to 40 μm , and a short side (S) of 2 to 30 μm , preferably 6 to 20 μm . The size of the flat singlefilament according to the present invention normally is 1 to 10 deniers (hereinafter abbreviated as "d"), preferably 2 to 5d. A flat singlefilament with a size less than 1d may have a problem with its strength not sufficient for its satisfactory processing into yarn and fabric, while the one, whose size is more than 10d, may cause a problem with the flexibility of the fabric resulting from it. The

total size of the multifilament yarn composed of flat singlefilaments according to the present invention is normally 10 to 100d, preferably 20 to 80d.

The shape of the cross-section of singlefilament according to the present invention includes, without limitation, ellipse, rectangle, W and hourglass. Among singlefilaments with cross-sections of these shapes, however, ones with a cross-section shaped like W or hourglass are preferable for the present invention, because such a shape allows the singlefilaments to fit in closely with one another when processed into a multifilament, which, in turn, can yield a fabric smooth in surface and small in thickness, contributing to its improved flexibility and higher EMI shielding performance. The average flat ratio of a multifilament useful in constructing the electrically conductive fiber material of the present invention refers to the value determined by drawing a rectangle circumscribed along the cross-section of the multifilament as illustrated in Fig. 2 and dividing the long side (l) of the rectangle by its short side (s), which is normally in the range of 1.0 to 8.0, preferably 1.2 to 7.0. A multifilament with an average flat ratio of less than 1.0 may cause a problem of increased thickness of the resultant fabric, adversely affecting its flexibility, as well as its EMI shielding performance, while the one, whose average compression is more than 8.0, has a problem with its processing into fabric, as well as with the

EMI shielding performance of the fabric.

The fabric surface occupancy ratio referred to in the present invention refers to the value determined for the warp and weft of fabric as illustrated in Fig. 4 according to the following formulas:

Fabric surface occupancy ratio (%) for warp

$$= \text{Warp width (A)} / \text{Warp pitch (B)} \times 100$$

Fabric surface occupancy ratio (%) for weft

$$= \text{Weft width (C)} / \text{Weft pitch (D)} \times 100$$

According to the present invention, electrically conductive fiber materials may preferably be manufactured using a fabric referred to in the present invention, the warp of which has a fabric surface occupancy ratio of 60 to 90% and the weft of which has a fabric surface occupancy ratio of 90 to 120%.

If the warp has a fabric surface occupancy ratio of less than 60%, slipping may occur, adversely affecting the EMI shielding performance of the electrically conductive material. If the warp has a fabric surface occupancy ratio of more than 90%, flattening of the weft may occur, adversely affecting the thickness of the electrically conductive material, as well as its EMI shielding performance.

If the weft has a fabric surface occupancy ratio of less than 90%, the size of openings at the intersections of the fabric would be increased, making it more subject to slipping with resultant deterioration in the EMI shielding

performance of the electrically conductive material. If the weft has a fabric surface occupancy ratio of more than 120%, the thickness would be increased, affecting uniform plating of the fabric with poor penetration of a plating solution through it.

According to the present invention, fabric may be finished by calendering to enable the fabric surface occupancy ratios of its warp and weft to be held within their respective ranges specified above.

The thermoplastic fiber useful in manufacturing the electrically conductive materials of the present invention includes, without limitation, polyester fiber such as polyethylene terephthalate fiber, polyamide fiber such as nylon 6 and nylon 66, and acrylic fiber. Among these fibers, however, polyester fiber is preferable for the present invention because it is advantageous in durability and ease of processing into flat single filament, multifilament and fabric.

The flat single filament of the present invention may be manufactured by methods including, but not limited to, calendering and melt spinning. Among these methods, however, the melt spinning method is preferable for the present invention because it can manufacture a single filament uniform in flatness. If a woven fabric is used as a substrate on which a metal coating layer is formed for manufacturing of the electrically conductive material of the present

invention, usually the fabric has a cover factor of 1000 to 3000, preferably 1500 to 2500.

Fabric with a cover factor of less than 1000 may has a problem of increased size of openings at the intersections of the fabric, resulting in deteriorated EMI shielding performance of the electrically conductive material. Conversely, fabric with a cover factor of more than 3000 may has a problem not only with its awkward manufacture, but also with its poor flexibility due to its high density, which also causes poor penetration of a plating solution through it, adversely affecting the ease of its plating and the durability of the resultant metal coating formed on it.

The cover factor of woven fabric referred to in the present invention is the value determined by its design factors - total warp size (D1), warp density (N1), total weft size (D2) and weft density (N2) according to the following formula:

$(D1)^{1/2} \times N1 + (D2)^{1/2} \times N2$, where the yarn size is expressed in deniers and the yarn density in yarns/inch.

Metal coating of fabric constructed of thermoplastic multifilament yarn composed of flat singlefilaments as referred to in the present invention to manufacture an electrically conductive material may be achieved by using methods such as spattering, vacuum deposition, electroplating and electroless plating that have

been disclosed in various prior art references for such coating. Among these methods, however, electroless plating is preferable for the present invention because it is advantageous in that it can metal-plate fabric with formation of a metal coating at the intersections of its yarns. Electroless plating of fabric according to the present invention may be carried out according to well-known procedure which has a step of applying a catalyst to the fabric, followed by a step of its chemical plating. For the catalyst applying step, the present invention may use either of the two known methods: one is by sensitizing fabric with an aqueous solution of tin chloride, followed by treatment of the fabric with an aqueous solution of palladium chloride, and the other is by applying a one-solution catalyst of tin-palladium colloid to fabric, followed by removal of tin ions on its colloidal surface layer for exposure of palladium effective as a catalyst for its chemical plating. The chemical plating process may be performed using plating bath and conditions known by those skilled in the art. The chemical plating bath normally contains a metal salt, reducer, buffer, pH controller and other agents necessary to achieve the purpose of the present invention.

Conductive metals useful in plating fabric to manufacture electrically conductive materials of the present invention includes, without limitation, silver, copper, nickel, cobalt and tin. Among these metals, however, copper

and nickel are preferable for the present invention because both metals are advantageous in providing a plating bath stable and easy to handle. The plating of fabric according to the present invention may preferably be carried out so that the thickness of the metal coating formed on the fabric is in the range of 0.05 to 5 μm .

Fabric plated with a metal coating thickness of less than 0.05 μm may fail to provide a sufficient surface conductivity to convert the fabric into an electrically conductive material referred to in the present invention. Conversely, fabric plated with a metal coating thickness of more than 5 μm may fail to show any further increase in its surface conductivity due to such a thick metal coating, which only contributes to its deteriorated flexibility.

In general, metal plating of any substrate is evaluated for a degree of metal coating formed on the substrate in terms of metal deposition per unit area or surface resistance more often than in terms of thickness. In this respect, the metal plating of fabric according to the present invention may be performed so that the fabric has a metal deposition of 5 to 50 g/m^2 , preferably 10 to 30 g/m^2 , and a surface resistance of 0.001 to $1\Omega/\square$, preferably 0.01 to $0.1\Omega/\square$.

[Examples]

The present invention will be understood more clearly with reference to the following Examples; however,

these examples are intended to further illustrate the present invention and are not to be construed to limit the scope of the present invention.

[Evaluation]

The electrically conductive materials obtained according to Examples 1 and 2, and Comparative Example 1 were evaluated for three items - surface conductivity, EMI shielding performance and flexibility - according to their respective evaluation methods described below. The results of the evaluation are shown in Table 1 .

1. Surface conductivity

A resistance measuring device (Mitsubishi Chemical Corporation-made Loresta-EP MCP-T360) was used to measure each test sample for surface conductivity in Ω/\square according to the four-terminal four-probe measurement method (specified by JIS-K-7194).

2. EMI shielding performance

① 10 MHz to 1GHz region

A measuring cell similar to the one devised by Kansai Electronic Industry Development Center (KEC)'s Ikoma Testing Station was prepared to receive 10MHz to 1GHz generated from a spectrum analyzer with a tracking generator (Agilent Technology-made HP8591EM) at the measuring cell's receiving unit through a test specimen of the fabric set in the cell to measure its EMI shielding

performance in dB over the 10 MHz to 1GHz region with the spectrum analyzer

② 1GHz to 15GHz region

A steel shielding box with an internally-built double rigid horn antenna (EMCO-made EMCO3115) was prepared according to MIL-STD-285 in such a way that the box was provided with an opening on one face, over which a test specimen of the fabric was attached, to receive the radio waves of 1GHz to 15GHz generated with a synthesized signal generator (Agilent Technology-made HP83731A) at the internal antenna through the test specimen from another double rigid horn antenna (EMCO-made EMCO3115) at the opposite position outside the box so as to measure the specimen's EMI shielding performance in dB over the 1GHz to 15GHz region with a spectrum analyzer (Agilent Technology-made HP8563E).

③ Flexibility

JIS-L-1096 Method A (known as 45° Cantilever Method) was used to measure a test specimen of the fabric in mm for evaluation of its flexibility.

[Example 1]

A plain weave fabric with 50 denier (hereinafter abbreviated as "d")-24 filament (hereinafter abbreviated as "f") regular polyester multifilament textured yarn for its warp and 75d-36f polyester multifilament yarn (composed of

singlefilament with a W-shaped cross-section, whose circumscribed rectangle has a long side (L) of $35\text{ }\mu\text{m}$ and a short side (S) of $15\text{ }\mu\text{m}$ - Asahi Chemical-made Technofine) for its weft was scoured, dried and heat-preset and subjected to a surface etching treatment by caustic hydrolysis for weight reduction by 10% to convert the fabric into one with a warp density of 123 yarns/inch, a weft density of 84 yarns/inch and a cover factor of 1597.

The fabric was immersed in an aqueous solution containing 0.3g/L of palladium chloride, 30g/L of stannous chloride and 300ml of 36% hydrochloric acid at 40°C and then washed with water. Thereafter, the fabric was immersed in a solution of borofluoric acid with an acid concentration of 0.1N and then washed with water. The fabric was subsequently immersed in an electroless copper plating bath consisting of 7.5g/L of copper sulfate, 30ml/L of 37% formalin and 85g/L of Rochelle salt and then washed with water. The copper-plated fabric was further immersed in an electroless nickel plating bath containing 300g/L of nickel sulfamate, 30g/L of boric acid and 15g/L of nickel chloride at a pH of 3.7 with a current density of 5A/dm^2 to build up a nickel layer on it before washing it with water to obtain an electrically conductive material with a metal coating layer consisting of 25g/m^2 of copper and 5g/m^2 of nickel. The metal coated textile material was subjected to the above-mentioned evaluation, the result of which is as shown in Table 1.

[Example 2]

A plain weave fabric with 30d-10f polyester multifilament yarn (composed of singlefilament with a W-shaped cross-section, whose circumscribed rectangle has a long side (L) of 35 μ m and a short side (S) of 15 μ m - Asahi Chemical-made Technofine) for its warp and 50d-30f polyester multifilament yarn (composed of singlefilament with a W-shaped cross-section, whose circumscribed rectangle has a long side (L) of 35 μ m and a short side (S) of 15 μ m - Asahi Chemical-made Technofine) for its weft was scoured, dried and heat-preset before being caustic treatment for weight reduction by 10% to convert the fabric into one with a warp density of 149 yarns/inch, a weft density of 138 yarns/inch and a cover factor of 1792.

The fabric was immersed in an aqueous solution containing 0.3g/L of palladium chloride, 30g/L of stannous chloride and 300ml of 36% hydrochloric acid and then washed with water. Thereafter, the fabric was immersed in a solution of borofluoric acid with an acid concentration of 0.1N and then washed with water. The fabric was subsequently immersed in an electroless copper plating bath consisting of 7.5g/L of copper sulfate, 30ml/L of 37% formalin and 85g/L of Rochelle salt and then washed with water. The copper-plated fabric was further immersed in an electroless nickel plating bath consisting of 300g/L of nickel sulfamate, 30g/L of boric acid and 15g/L of nickel chloride at a pH of 3.7 with a current

density of $5A/dm^2$ to build up a nickel layer on it before washing it with water to obtain an electrically conductive material with a metal coating layer consisting of $25g/m^2$ of copper and $5g/m^2$ of nickel. The metal coated material was subjected to the above-mentioned evaluation, the result of which is as shown in Table 1.

[Comparative Example 1]

A plain weave fabric with 50d-36f regular polyester multifilament textured yarn for its warp and weft was scoured, dried and heat-preset before being caustic treatment for weight reduction by 10% to convert the fabric into one with a warp density of 164 yarns/inch, a weft density of 104 yarns/inch and a cover factor of 1895.

The fabric was immersed in an aqueous solution containing 0.3g/L of palladium chloride, 30g/L of stannous chloride and 300ml of 36% hydrochloric acid and then washed with water. Thereafter, the fabric was immersed in a solution of borofluoric acid with an acid concentration of 0.1N and then washed with water. The fabric was subsequently immersed in an electroless copper plating bath consisting of 7.5g/L of copper sulfate, 30ml/L of 37% formalin and 85g/L of Rochelle salt and then washed with water. The copper-plated fabric was further immersed in an electroless nickel plating bath consisting of 300g/L of nickel sulfamate, 30g/L of boric acid and 15g/L of nickel chloride at a pH of 3.7 with a current density of $5A/dm^2$ to build up a nickel layer on it before

washing it with water to obtain an electrically conductive material with a metal coating layer consisting of 20g/m² of copper and 5g/m² of nickel. The metal coated material was subjected to the above-mentioned evaluation, the result of which is as shown in Table 1.

Table 1

		Example 1	Example 2	Comparative Example 1
Fabric thickness (μ m)		75	80	120
Flat ratio (%)	Warp	2.9	3.6	2.0
	Weft	5.9	5.0	3.2
Fabric surface occupancy ratio (%)	Warp	76	69	86
	Weft	92	119	70
Surface conductivity (Ω/\square)		0.015	0.036	0.056
EMI shielding Performance (dB)	10MHz	100	102	96
	50MHz	97	92	83
	100MHz	91	85	76
	500MHz	83	76	66
	1GHz	82	75	65
	5GHz	80	70	60
	10GHz	84	74	63
	15GHz	78	74	63
Flexibility (mm) (warp/weft)		55/42	37/37	75/45

[Effects of the Invention]

As can be seen from Table 1 fabric constructed of multifilament yarn composed of flat singlefilaments with an average compression of 1.5 to 5, allowing the multifilament yarn to have an average of 1.0 to 8.0, when chemically plated with metal, can yield an electrically conductive material small in thickness with a metal coating layer, whose surface is fine, uniform and smooth, maintaining the flexibility of the fabric and showing high EMI shielding performance over a wide frequency range.

[Brief Description of the Drawings]

Fig. 1 is a conceptual cross-sectional view of the flat singlefilament of the present invention for calculation of its compression.

Fig. 2 is a conceptual cross-sectional view of the multifilament yarn of the present invention for calculation of its compression.

Fig. 3 is a photo showing the surface of the woven fabric used in the examples of the present invention.

Fig. 4 is a conceptual schematic illustration of the warp and weft of the present invention for calculation of their respective fabric surface occupancy ratios.

[Legends]

- 1 ... Singlefilament
- 2 ... Warp multifilament yarn
- 3 ... Weft multifilament yarn

A ... Warp multifilament yarn width

B ... Warp pitch

C ... Weft multifilament yarn width

D ... Weft pitch